

Table 8 Comparison of optical spectroscopy techniques for silicon analysis

Technique/Reference	Sample interaction	Application
Fourier transform infrared Room temperature [171-174] Low temperature [175-177]	Infrared absorption	Oxygen in CZ silicon quantified at ppm level Ppb sensitivity to dopants and impurities in Si
Photoluminescence Room temperature [175,178] Low temperature [175,179-184]	Light emission	Spatial signal mapping of compound semiconductors Sub-ppb sensitivity to dopants and electrically active impurities

or no background. This applies to all elements in the periodic table, including H, C, and O, although these are also common contaminants found in the vacuum environment. Only about 0.01-5% of the sputtered atoms and molecules are in an ionized state, but these can be effectively collected and focused. Surface sensitivity to organic and inorganic contaminants is the real strength of ToF-SIMS. The technique is fundamentally different from dynamic SIMS, in that it can be applied in a depth profiling mode to ultra thin films (<10 nm) at the surface. It is not uncommon to find a higher current Cs⁺ ion source mounted on the same analysis station as the conventional Ga⁺ one to permit accelerated etching between spectral acquisitions.

The ion sputtering process can be understood in qualitative terms, but it is difficult to predict and model in detail. Because of sputter artifacts and a six order-of-magnitude spread in sensitivity to elements in the periodic table, it is burdensome to carry out quantitative analysis without recourse to a set of carefully prepared reference standards. Ideally, these must be as close to the unknown as possible, both in dopant or impurity level, and in matrix composition. In the optimum case, precisions near 1-5% can be realized. Even so, pitfalls remain, as outlined in a number of comprehensive reviews [167-170]

2. Optical Spectroscopy

Purpose: The primary optical techniques for high sensitivity detection of dopants and impurities in semiconductor solids are Fourier transform infrared (FTIR) and photoluminescence (PL) spectroscopies. These reach parts-per-billion-atomic (ppba) and lower when performed at temperature near 4-15°K. FTIR

works best for bulk silicon which is transparent in the infrared, and is frequently applied even at room temperature for the quantification of oxygen and carbon in Czochralski (CZ) silicon crystals and wafers. PL at visible light frequencies penetrates only about 0.5-5 μm into silicon, and hence is suitable for the analysis of epitaxial films. In some applications, low temperature PL reaches sub-parts-per-trillion-atomic (ppta) detectability. A comparison of the methods is given in Table 8.

Methods: Infrared spectroscopy is based on the fact that molecules have discrete absorption frequencies associated with their vibrational and rotational motions. When a sample is placed in infrared light, it will selectively absorb at those resonant frequencies of the dopant or impurity species and pass the remainder. The absorption is associated with a change in the dipole moment of the molecule.

The transmittance (T_s , expressed in wavenumbers) for a normal incidence infrared probe on a double-side polished silicon slab of thickness d is given by

$$T_s = [(1 - R)^2 \exp(-\alpha d)] / [1 - R^2 \exp(-2 \alpha d)] \quad (28)$$

where R is the internal surface reflectivity and α the absorption coefficient.

For determination of interstitial oxygen in Czochralski silicon for example, the 1107 cm⁻¹ band related to stretching modes of Si-O bonds in the Si₂O molecule is measured [171,172,177]. Infrared transmission (T_F) through a float zone slab of the same thickness d (as before) combined in ratio with [28] yields

$$T = T_s / T_F \sim \exp[-(\alpha_s - \alpha_F)d] = \exp(-\alpha_0 d) \quad (29)$$